

UNPUBLISHED PRELIMINARY DATA

INVESTIGATION OF ELECTROCALORIC EFFECTS
IN FERROELECTRIC SUBSTANCES

Status Report No. 2

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DEFINITION OF TERMS AND SYMBOLS

Rationalized MKS units are used throughout. Thermodynamic formulas such as $dy = Tds + Xdx + EdP$ are written for a unit volume of material. This procedure is not exactly proper because the thermodynamic system (the experimental crystal) changes its volume slightly, but only inappreciable errors result.

C = Curie constant. Curie-Weiss Law is $\chi = C/(T - T_p)$.

c_E = Specific heat at constant field (and zero stress).

c_P = Specific heat at constant polarization (and zero stress).

D = Electric displacement. $D = \epsilon_0 E + P$.

E = Applied electric field.

G_1 = Elastic Gibbs function. $G_1 = U - TS - xX$.

P = Electric polarization per volume. P_s is the spontaneous electric polarization per volume.

$G_{10} = G_1$ at some (arbitrary) reference temperature.

p^E = Pyroelectric coefficient at constant field (and stress).

S = Entropy per volume.

T = Temperature in degrees Kelvin.

T_c = Critical temperature (loosely speaking, either T_f or T_p).

T_f = Ferroelectric Curie temperature = the temperature at which P_s disappears when the substance is heated.

T_p = Paraelectric Curie temperature as defined by the Curie-Weiss Law,
 $\chi = C/(T - T_p)$.

U = Internal energy per volume.

X = Applied stress. (Tensile stress has a positive sign.)

x = Strain. (Elongation has a positive sign.)

ϵ_0 = Electric permittivity of vacuum = 8.85×10^{-12} coul²/n.m².

ζ = Devonshire's sixth-order coefficient (of P^6) in G-expansion.

ξ = Devonshire's fourth-order coefficient (of P^4) in G-expansion.

(ψ appears as a misprint in place of ξ in Eq. 7 and 9 of Status Report No. 1.)

ρ = Mass density.

χ = Electric susceptibility. $dP = \epsilon_0 \chi dE$. The symbol χ may carry subscripts such as p (paraelectric), f (ferroelectric), or superscripts such as T (constant temperature), X (constant stress), etc.

ψ = The non-linear polarization term in the Devonshire expansion. Usually written $\psi(P)$.

ψ' = The derivative of $\psi(P)$ with respect to P. Usually written $\psi'(P)$.

ω = Devonshire's second-order coefficient (of P^2) in G-expansion.

Note: Equations in the two Status Reports are numbered in order beginning with those in Status Report No. 1.

SUMMARY OF STATUS REPORT NO. 1

Status Report No. 1 contained a thermodynamic description of the electrocaloric effect, the pyroelectric effect, and the relationship between them.¹ It was shown that the same crystalline properties give rise to both effects and that the relevant thermodynamic coefficients can be determined from electrocaloric measurements. So-called "tertiary effects" which arise from inhomogeneous temperatures or fields can be so large as to mask the "real" effects; the tertiary effects are more easily eliminated in the electrocaloric than in the pyroelectric measurements.

The apparatus and techniques that were devised for accurately regulating the temperature of the experimental chamber and making simultaneous measurements of the changes in electric polarization and temperature that occur with changes in applied field were described.

PHENOMENOLOGICAL DESCRIPTION OF KH_2PO_4

The electrocaloric effect above the Curie temperature can be expressed in terms of the Curie-Weiss Law and the electrocaloric effect can be used to determine the Curie constant. The Curie-Weiss Law can be written

$P = \epsilon_0 C E / (T - T_p)$, then $(\partial E / \partial T)_P = P / \epsilon_0 C$ and Eq. (2) becomes

$$1/\epsilon_0 C = (\rho c_p / T P) (\partial T / \partial P)_S \quad (25)$$

which for small changes in T produced by the electrocaloric effect becomes

$$1/\epsilon_0 C = (2\rho c_p/T)(\Delta T/\Delta P^2). \quad (26)$$

The electrocaloric measurements can also be expressed in terms of the coefficients used to express free energy of the crystal. The most usual expansion of a free energy function for a ferroelectric substance is the sum of a temperature-dependent term plus a power series of polarization terms. Such an expression for the elastic Gibbs function is

$$G_1 = G_{10} + \omega P^2/2 + \xi P^4/4 + \zeta P^6/6 + \dots \quad (8)$$

Various attempts² to fit the experimental data for KH_2PO_4 to this particular function have not succeeded. A more general expansion has been used by Devonshire³, Kanzig⁴ and others; therefore, we write for KH_2PO_4 in lieu of Eq. (8)

$$G_1 = G_{10} + \omega P^2/2 + \psi(P) \quad (27)$$

for the unstressed crystal where ω is a function of temperature and $\psi(P)$ is a saturation function which can in principle be obtained from experiment. From Eq. (7), $dG_1 = -SdT - x dX + EdP$, so that at zero stress,

$$E = (\partial G_1/\partial P)_T = \omega P + \psi'(P). \quad (28)$$

Kanzig⁴ has shown that Baumgartner's data for the narrow temperature range from the Curie temperature to 4° above the Curie temperature agree with Eq. (28); he shows that the linear term ω is $(T - T_p)/\epsilon_0 C$ in conformity with the Curie-Weiss Law and he presents an experimental curve for the saturation function $\psi'(P)$.

Since ω is the only temperature-dependent term in Eq. (28), $(\partial E/\partial T)_P = (\partial \omega/\partial T)_P P$, and Eq. (2) for the electrocaloric effect becomes

$$dT = (T/\rho c_p)(\partial \omega/\partial T)_P P dP. \quad (10)$$

If the temperature change is small, $(\partial\omega/\partial T)_P$ can be expressed in terms of electrocaloric measurements as

$$(\partial\omega/\partial T)_P = (2\rho c_P/T)(\Delta T/\Delta P^2), \quad (29)$$

the right-hand side of this expression being identical to that of Eq. (26). The value of ω at the paraelectric Curie temperature is known to be practically zero because the Curie-Weiss Law gives infinite susceptibility at this temperature so that ω can be determined from the electrocaloric measurements.

A relationship between the electrocaloric effect and the pyroelectric effect is shown by comparing the expressions for the electrocaloric and pyroelectric effects, Eq. (4) and (19). For conditions of zero stress,

$$dT = -(T/\rho c_E)(\partial P/\partial T)_E dE \quad (4)$$

$$dP = (\partial P/\partial E)_T dE + (\partial P/\partial T)_E dT \quad (19')$$

Thus the pyroelectric coefficient, $p^E = (\partial P/\partial T)_E$, can be determined from electrocaloric measurements.

EXPERIMENTAL PROCEDURE

The sandwich-like crystal mount shown in Fig. 1 and described in Status Report No. 1 was not successful for potassium dihydrogen phosphate (KH_2PO_4) despite the fact that a similar mount had been successfully used for Rochelle salt⁵. We found that large fields, particularly a-c fields, caused KH_2PO_4 crystals to shatter when they were cooled below the Curie temperature. This shattering was probably caused by the large piezoelectric stresses between the two plates and the cement between them. After several such failures the crystals were mounted without cement. With this arrangement the piezoelectric strains during the course of the experiment caused a cumulative slippage of one crystal with respect to the other until the high voltage lead would be short-circuitual to one of the central electrodes. Moreover, at a pressure of 10^{-7} torr these crystals which were about 3 mm thick would sustain an arc across their edges at about 1,000 volts.

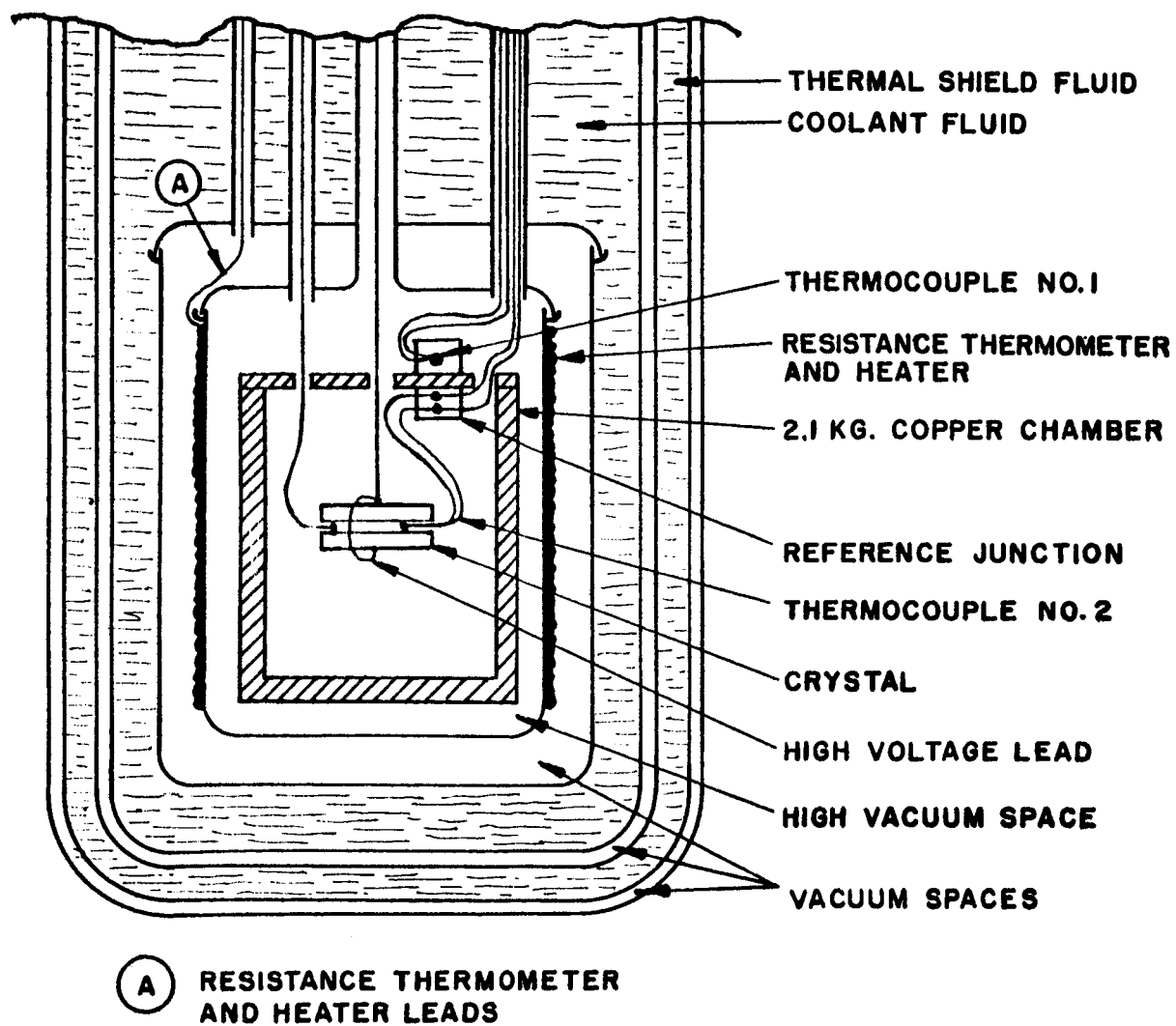


FIG.1 CONSTANT TEMPERATURE CHAMBER

The method finally resorted to was to mount a single crystal, 1.393 mm x 2.385 mm x 2.974 mm, in a horizontal position by means of cotton threads. The copper-constantan thermocouple was cemented to the lower face with an insulating film of formvar-alcohol-toluene. Arcing was prevented at the highest direct fields used (428 kv/m) by adding helium gas at atmospheric pressure. Applied alternating voltages were kept below 25 volts. Unfortunately the helium gas greatly increased the heat loss by the crystal which meant that only the "instantaneous" changes in temperature could be measured. The recorder would record the largest temperature change observed in about one second; this is fast enough to permit identification and elimination of spurious effects due to such things as occasional switching pulses and non-adiabatic conditions.

The noise level on the recorder was about ± 0.5 div and the temperature sensitivity was about 4.4×10^{-4} deg/div on the most sensitive scale used. The heat capacity of the electrodes, thermocouples, thread, and cement was small compared to the heat capacity of the crystal. The circuits for simultaneously recording the electrocaloric temperature changes and the changes in electrical polarization that accompany changes in the applied field are shown in Fig. 2. (This drawing shows the sample as a sandwich instead of the single slab actually used.)

At each temperature several cycles of polarization were traversed in order to establish steady-state conditions before usable data were taken. After that, two types of measurements were made: (1) "single-step" measurements in which the field was switched completely on or off, and (2) "point-by-point" measurements in which the hysteresis cycle was traversed in a series of pre-determined steps. Each field step required about one second, fast enough to insure adiabatic processes but slow enough to avoid sudden crystalline strains or spurious electrical pulses. The steps were spaced two minutes apart. Unfortunately, the gas which was admitted to the chamber to prevent arcing caused an appreciable heat leak which of course was ignored in determining the cumulative electrocaloric temperature changes from the strip-chart recorder. This heat leak affected the thermocouple temperature which was attached to the surface of the crystal rather than the temperature of the specimen as evidenced by the agreement between cumulative step-by-step values of the polarization and the single-step value. Fig. 3 and Fig. 4 are

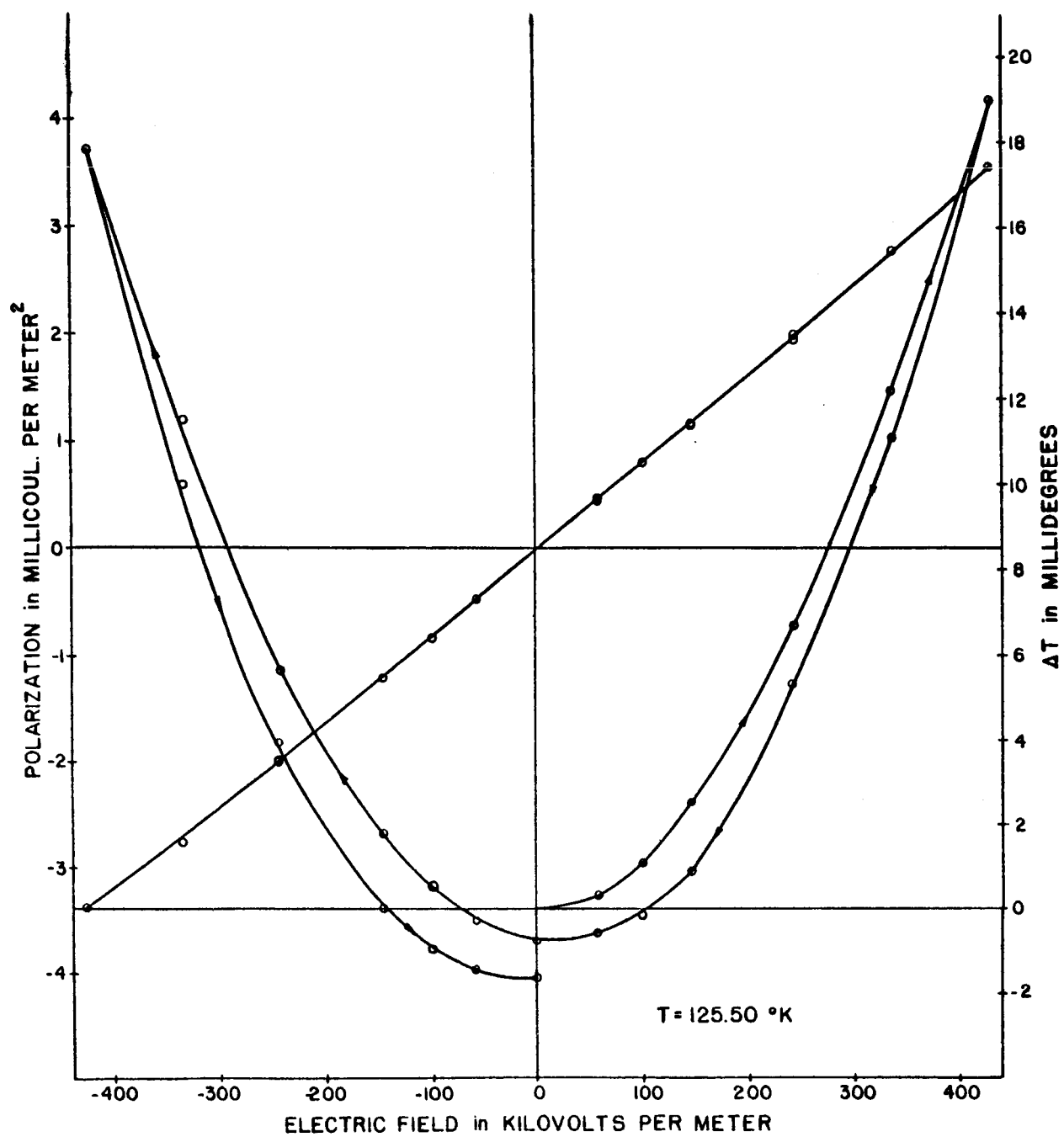


FIG. 3 DIELECTRIC & ELECTROCALORIC MEASUREMENTS ABOVE THE CURIE TEMPERATURE

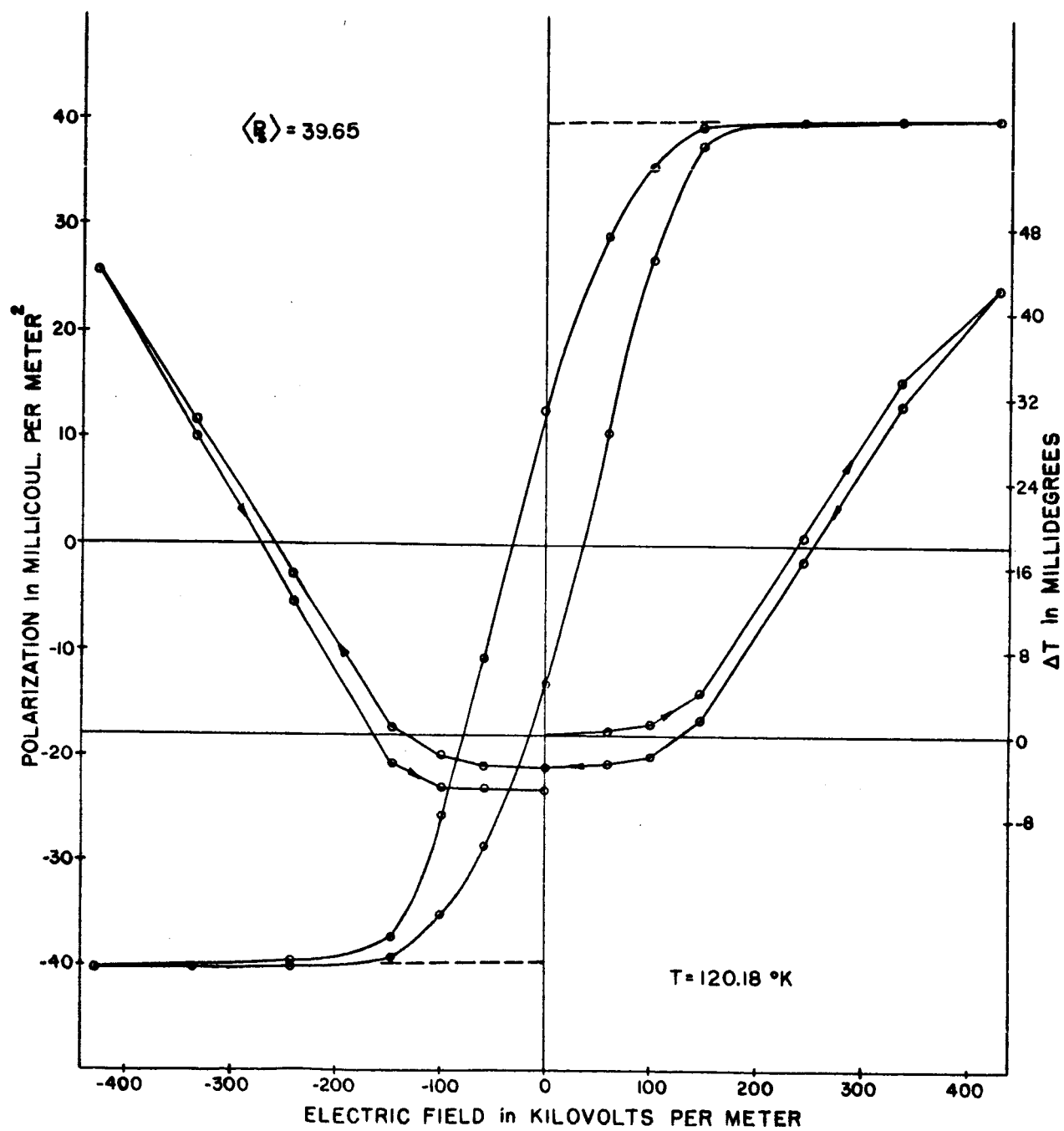


FIG. 4 DIELECTRIC & ELECTROCALORIC MEASUREMENTS BELOW THE CURIE TEMPERATURE

representative of the point-by-point electrocaloric measurements made above and below the Curie temperature.

MEASUREMENTS OF KH_2PO_4 ABOVE THE CURIE TEMPERATURE

Our measurements in the paraelectric region (e.g., Fig. 3) gave practically linear relationships between P and E up to the highest fields used (428 kv/m) and at temperatures down to within a few tenths of a degree of the Curie temperature.

With the use of Eq. (26) in mind, experimental values of the electrocaloric temperature change ΔT were plotted against ΔP^2 for each temperature with the results shown in Fig. 5. Note that in the paraelectric region, 123°K and above, the curves are straight lines which intersect the origin, all in agreement with Eq. (26). This equation together with the density of the crystal ($\rho = 2.32 \text{ kg/m}^3$) and the specific heat at constant polarization ($c_p = 511 \text{ joules/kg deg}$)⁶, yields values for $1/\epsilon_0 C$ that are in fair agreement the value computed from Baumgartner's data⁷. The open circles in Fig. 6 represent the values of $1/\epsilon_0 C$ determined from Eq. (26); the solid line represents Baumgartner's average value.

Of course our dielectric data also yield a value for $1/\epsilon_0 C$. Each of the points of Fig. 7 represents a value of $\partial E/\partial P$ (or $1/\epsilon_0 \chi$) determined from the slope of a P vs E curve (e.g., Fig. 3) at a particular temperature. The slope of the line in Fig. 7 yields an average value of $1/\epsilon_0 C$; this value corresponds to $C = 3330 \text{ deg}$. and is shown by the broken line of Fig. 6. The agreement is as good as can be expected without applying a correction to convert our nearly adiabatic values to isothermal values.

The intersection of this line in Fig. 7 with the temperature axis is T_p the paraelectric Curie temperature 122.22°K ; it is somewhat lower than the ferroelectric Curie temperature T_f . This discrepancy is not uncommon for ferroelectric (and ferromagnetic) substances.

Since the right-hand side of Eq. (26) is identical to that of Eq. (29); i.e.,

$$1/\epsilon_0 C = (2\rho c_p/T)(\Delta T/\Delta P^2) \quad (26)$$

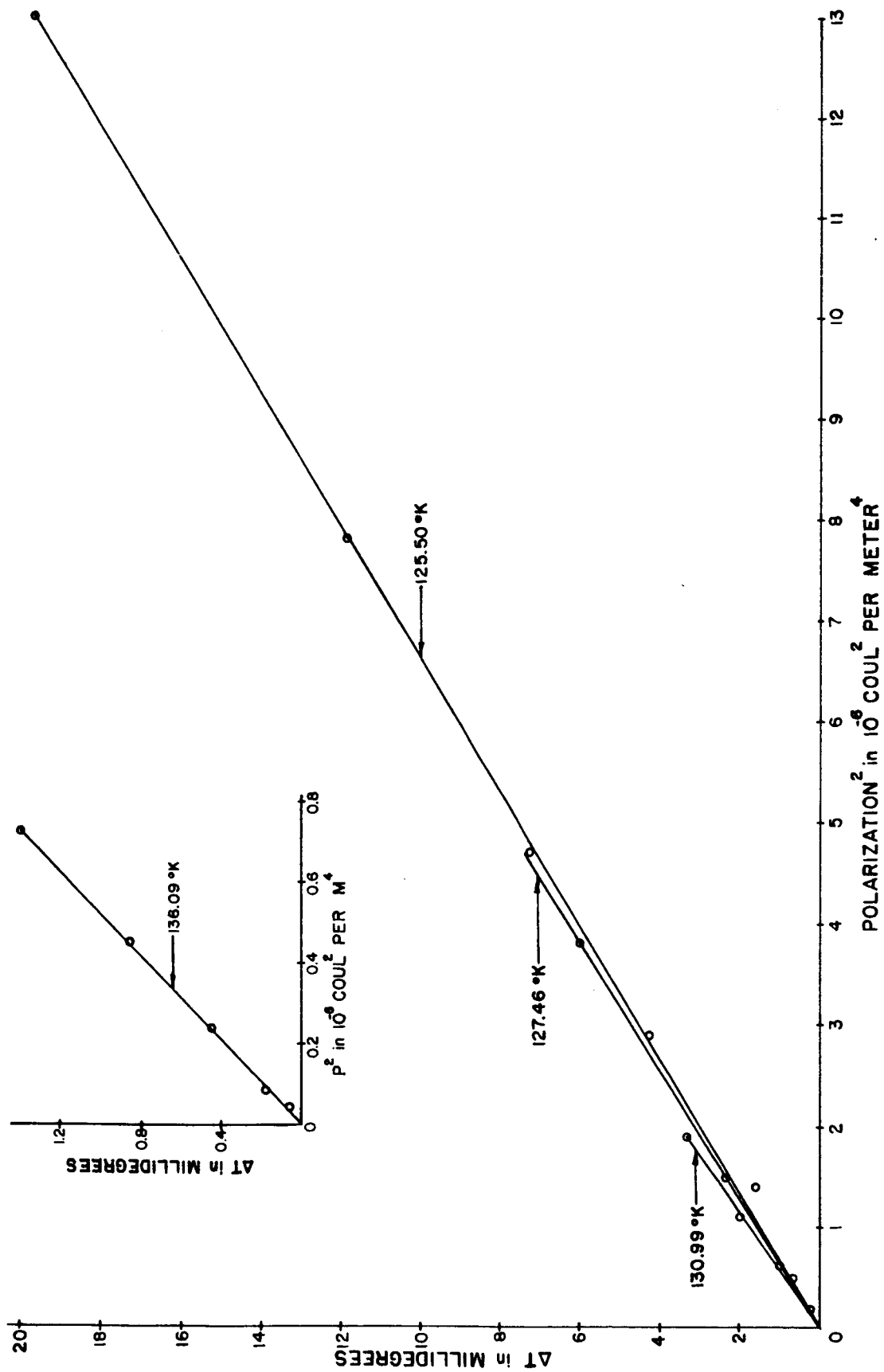


FIG. 5 ΔT vs. ΔP^2 ABOVE THE CURIE TEMPERATURE

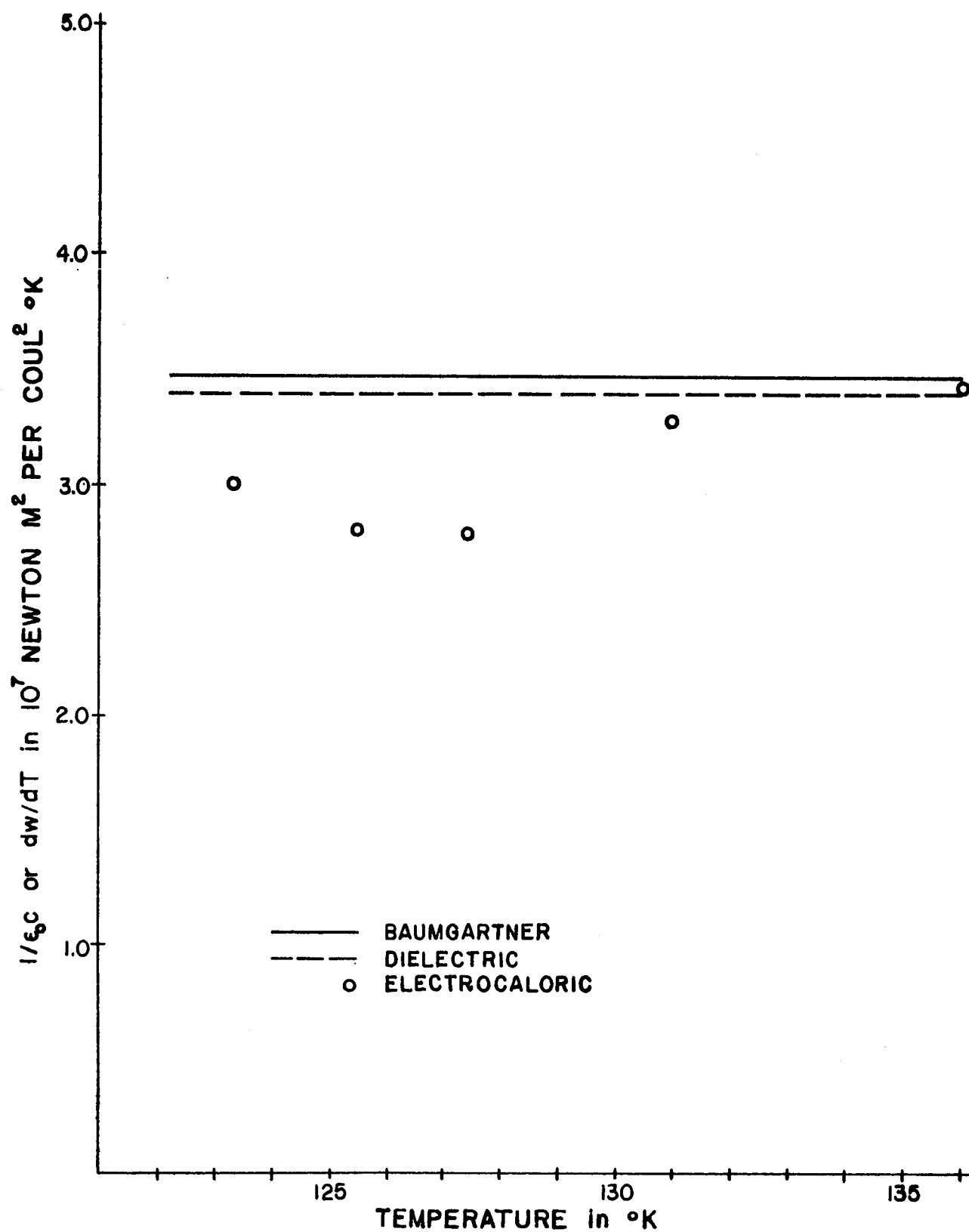


FIG. 6 ELECTROCALORIC MEASUREMENTS RELATED TO DIELECTRIC MEASUREMENTS ABOVE THE CURIE TEMPERATURE

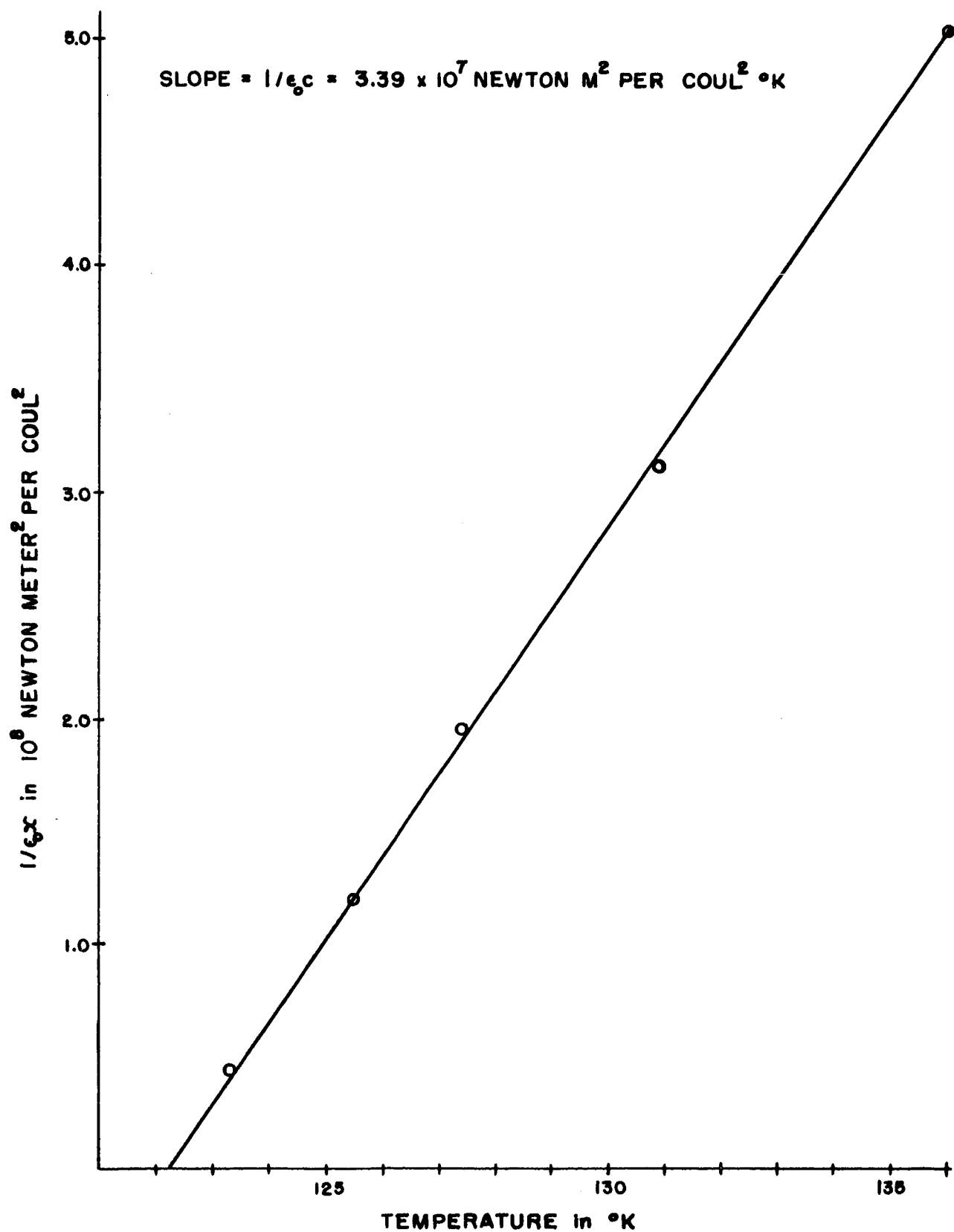


FIG. 7 A CURIE-WEISS PLOT OF
ELECTROCALORIC MEASUREMENTS

$$(\partial\omega/\partial T)_P = (2\rho c_P/T)(\Delta T/\Delta P^2), \quad (29)$$

then the relationship between the electrocaloric effect and the coefficient ω in the free energy expansion is already established. Fig. 6 gives the values of $\partial\omega/\partial T$. Now ω is the coefficient of the linear term in Eq. (28) and it must be practically zero at the Curie temperature, so the value of ω in the paraelectric region is established.

At first thought one would expect neither electrocaloric nor pyroelectric effects with a ferroelectric crystal above its Curie temperature simply because P_s is zero. On the other hand, application of an electric field can produce a polarization that could counterfeit P_s in the paraelectric region. The pyroelectric coefficient computed by using the Curie-Weiss law is

$$p^E \equiv (\partial P/\partial T)_E = -\epsilon_0 C E / (T - T_p)^2 \quad (30)$$

Our observations of the electrocaloric effect in the paraelectric region are in reasonable agreement with those predicted by the Curie-Weiss Law so a pyroelectric effect should exist above the Curie temperature provided that an electric field is applied. The pyroelectric signal observed by the Sperry Microwave Group (their Fig. 12 and 13 on p. 4-23) for BaTiO_3 above the Curie temperature of 120°C was probably due to the application of a biasing field from the input of their amplifier. Their pyroelectric signal seems to be as large in the paraelectric region as in the ferroelectric region. Explanations for the lack of pyroelectric effects at the Curie temperature have been discussed.^{8,1}

MEASUREMENTS OF KH_2PO_4 BELOW THE CURIE TEMPERATURE

In comparing the results of typical electrocaloric measurements above and below the Curie temperature (Fig. 3 and 4 respectively), one notices that ΔT bears a parabolic relationship to E above the Curie temperature whereas it bears an approximately linear relationship to E below the Curie temperature, at least in the high-field region where the polarization

is nearly reversible. Such behavior conforms to the behavior of a substance that obeys the Curie-Weiss Law, $P = \epsilon_0 C_E / (T - T_p)$. Substituting the value of $(\partial P / \partial T)_E$ into Eq. (4) and integrating over a small temperature range gives

$$\Delta T = \epsilon_0 C_T \Delta E^2 / 2 \rho c_E (T - T_p)^2 \quad (31)$$

Fortunately, c_E and c_p are approximately equal above the Curie temperature.

Below the Curie temperature, on the other hand, the Curie-Weiss Law will obviously not serve as an equation of state. Nevertheless, Eq. (2) and (4) are still valid. With the use of a reasonable elastic Gibbs function, Eq. (28), we can get Eq. (29) or

$$\Delta T = (T / 2 \rho c_p) (\partial \omega / \partial T)_P (P_2^2 - P^2). \quad (29')$$

At a temperature below the Curie temperature, the value of polarization attained by a single domain crystal as the applied electric field is reduced to zero from some large value is P_s ; i.e., a plot of ΔT vs P^2 for electric depolarization should give a straight line which intersects the P^2 axis at P_s^2 . Fig. 8 shows such plots. Agreement with theory is seen to be good except at the lower temperatures where the lower segments (for small P and E) are curved. Such curvature is caused by irreversible wall motions which heat the crystal during depolarization. These irreversible segments should disappear as indeed they do as the Curie temperature is approached because the irreversible effects which give rise to hysteresis disappear. Extrapolation of the straight line portions of the curves of Fig. 8 give the values for P_s represented by solid circles of Fig. 9. The agreement between the values obtained from electrocaloric and the hysteresis data are excellent; actually, the electrocaloric data require less extrapolation and give their best values for P_s near the Curie temperature, the very region where hysteresis data require a less certain extrapolation. Consequently, the ferroelectric Curie temperature T_f (the temperature at which the spontaneous polarization disappears) can be accurately determined from electrocaloric measurements. The ferroelectric Curie temperature given by the electrocaloric data is 123°K .

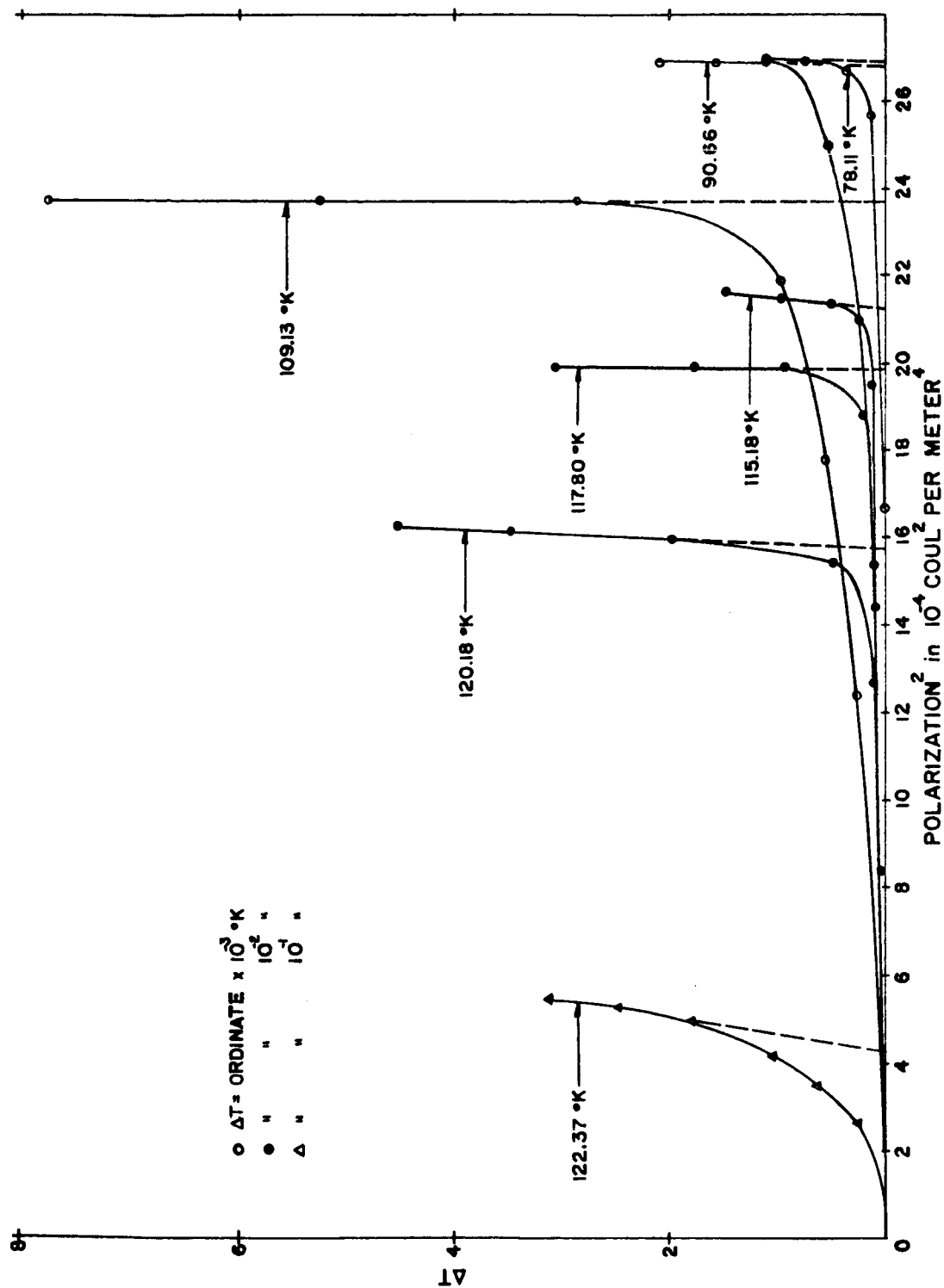


FIG. 8 ΔT vs ΔP^2 BELOW THE CURIE TEMPERATURE

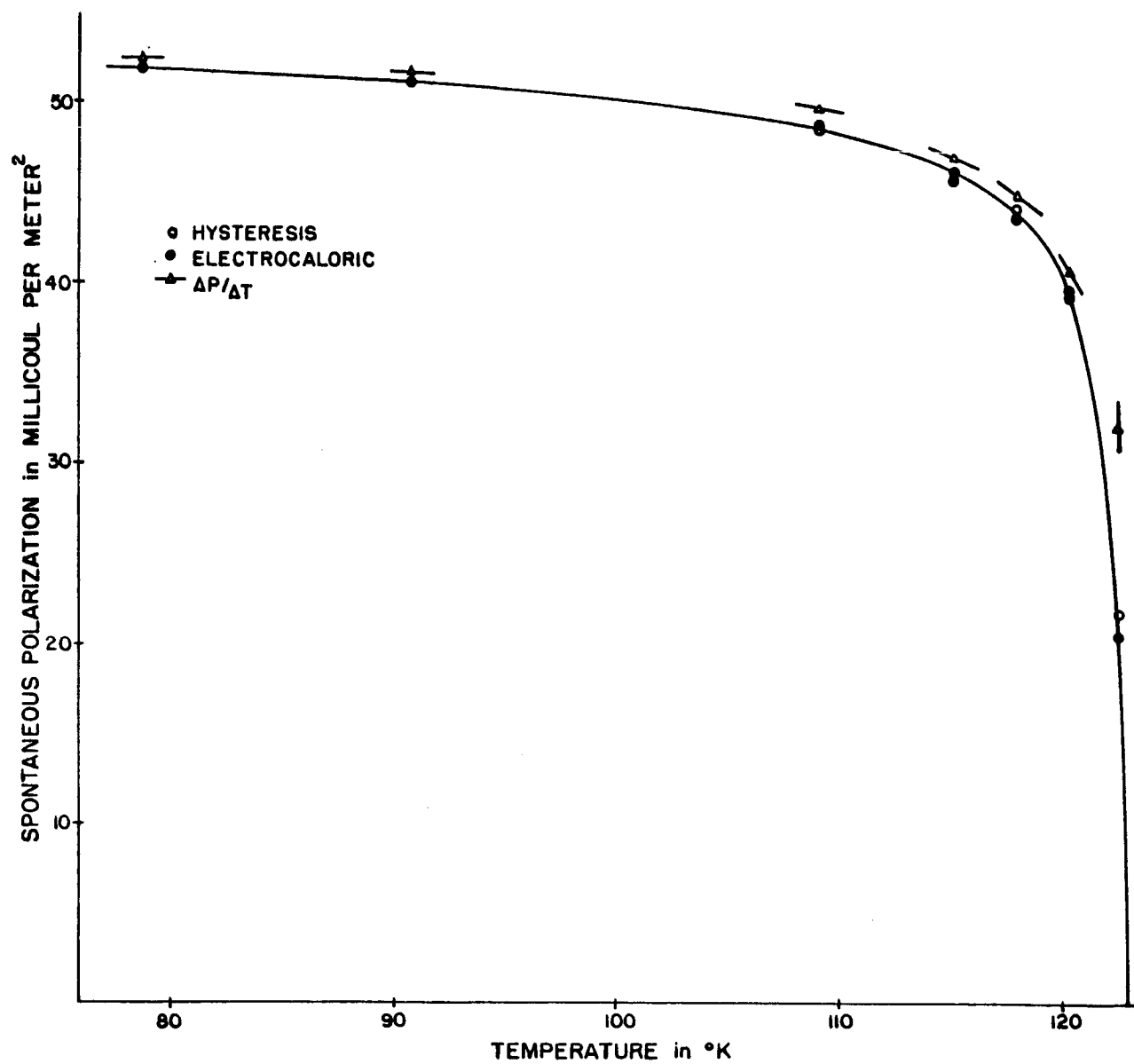


FIG. 9 SPONTANEOUS POLARIZATION & $\Delta P/\Delta T$ vs. TEMPERATURE

If the electrocaloric temperature changes are small compared to T and if $(\partial P/\partial T)_E$ does not change too much with the applied field E , measurements of the electrocaloric effect will give, via Eq. (4), values of $(\partial P/\partial T)$ directly; these values can then be compared to the values of $(\partial P/\partial T)$ determined from dielectric measurements; in particular the values of P_s vs T . Fig. 9 shows the results of such a comparison; the short lines represent values of $\Delta P/\Delta T$ obtained from the electrocaloric measurements. The value of density ρ used in this computation was $2.32 \times 10^3 \text{ kg/m}^3$; the values for the specific heat were obtained from Stephenson and Hooley.⁶ The values of P and T (the open triangle) through which the corresponding values representing $\Delta P/\Delta T$ have been drawn are located slightly above the P_s vs T curve because the measurements were made in the reversible region near the ends of the hysteresis loops. The agreement between the electrocaloric values of $(\partial P/\partial T)_E$ and the slope of the P_s vs T curve is good. These results indicate that the measurements are reasonably free from errors associated with non-adiabatic conditions and spurious effects due to large piezoelectric strains, and they show that unlike Rochelle salt⁵ the value of $(\partial P/\partial T)_E$ is approximately independent of the electric field even very close to the Curie temperature.

These data are not sufficiently accurate to permit us to determine $d\omega/\partial T$ in the ferroelectric region as we had intended to do by the use of Eq. (29),

$$\partial\omega/\partial T = (2\rho c_p/T)(\Delta T/\Delta P^2). \quad (29)$$

The inaccuracy is not attributable to the measurement of temperature but to the measurement of charge (i.e., polarization). A glance at Fig. 4 or Fig. 9 shows that an order-of-magnitude improvement in sensitivity would be necessary to obtain meaningful values for ΔP^2 in the reversible region where P changes very slowly with E . The behavior of ω as the crystal is cooled through the Curie temperature is crucial to the theory which is based on the assumption that the same free energy function (taken here to be the elastic Gibbs function) describes the properties of the crystal right on through the Curie temperature by a continuous change in the parameter ω . Consequently, we will try again to make these measurements.

Fortunately, the electrocaloric measurement of the pyroelectric coefficient $p^E = (\partial P / \partial T)_E$ does not involve measurements of P . It can be determined from the measurement of the electrocaloric temperature change and the applied field; i.e., from Eq. (4) for small changes in temperature,

$$(\partial P / \partial T)_E = - (pc_E / T) (\Delta T / \Delta E) \quad (4)$$

Values of c_E can be obtained from the measurements of Stephenson and Hooley.⁶ The experimental values are presented in Fig. 10.

SUMMARY

Electrocaloric measurements of a single crystal of KH_2PO_4 were made from 78°K to 136°K with special attention being paid to the region close to the Curie temperature, 123°K.

The results above the Curie temperature were reasonably consistent with the phenomenological description proposed by Devonshire and others and the pyroelectric coefficient $(\partial P / \partial T)_E$ computed either from electrocaloric measurements or from dielectric measurements seems to be reliable in the paraelectric region.

Below the Curie temperature reliable values for the first Devonshire coefficient ω could not be obtained because the change of polarization at high fields could not be measured with sufficient accuracy with the techniques used. Values for the pyroelectric coefficient were obtained in the ferroelectric region. As was pointed out in the Sperry Rand reports and in our Status Report No. 1, other properties in addition to the pyroelectric coefficient are important in determining the efficacy of a material as a pyroelectric detector.

PERSONNEL

Project Supervisor: G. G. Wiseman

Graduate Student Assistants: J. A. Hostetter and J. E. Smith

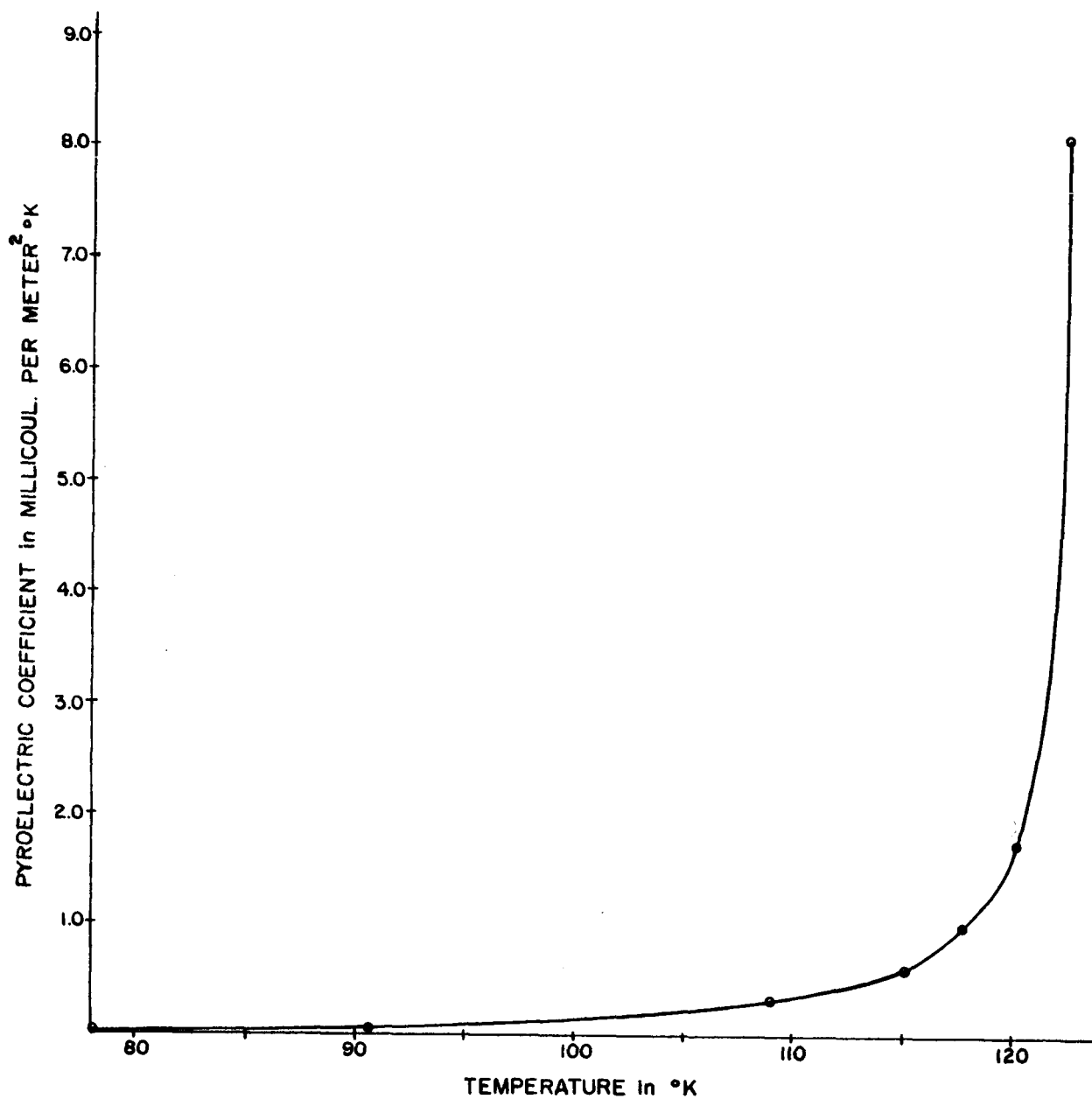


FIG.10 ELECTROCALORIC MEASUREMENT OF THE
PYROELECTRIC COEFFICIENT vs. TEMP.

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